

ENAMELS

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DEVELOPMENT OF A GLASS MATRIX COMPOSITION FOR LIGHT-COLORED HEAT-RESISTANT GLASS CERAMIC COATING FOR NICHROME ALLOYS

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The specifics of glass formation in the $R_2O - Al_2O_3 - SiO_3 - TiO_2$ multicomponent system ($R = Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}$) are considered. Regions of glass ceramic compositions are identified and the specifics of structure and phase formation of glass ceramic matrices are investigated. An optimum composition is determined, which can be used as a glass matrix for light-colored heat-resistant glass ceramic coating.

In the context of a market economy showing a dramatic increase in metal prices, the problem of protecting metal from high-temperature corrosion has become very significant.

Firing tools currently used in the production of enameled articles are based on nichrome alloys which become intensely oxidized at temperature 900°C and higher, and scale starts peeling off these tools after 50 h of service. This leads to rapid wear of the equipment, contamination of enameled products with scale, and, accordingly, their rejection.

An efficient way to protect firing tools from the effect of high temperatures is deposition of heat-resistant glass ceramic coatings [1].

Several researchers investigated this problem [1]. However, the resulting coatings usually contained chromophore oxides as heat-resistant fillers: Cr_2O_3 , NiO , CoO , Fe_2O_3 (USSR Inventor's certificates 358284, 542738) [2], which led to undesirable pigmentation of the enameled articles. Thus, the propensity of Cr_2O_3 to sublimation results in the fact that initially Cr_2O_3 sublimates from a heat-resistant coating (a firing tool) and then desublimates on the surface of the white enamel titanium coating of the product, and even in small quantities it can impart a disagreeable spotty yellowish-gray tint to the enamel that is being formed [2]. Since this effect must be eliminated, it is expedient to develop a light-colored heat-resistant glass ceramic coating not containing Cr_2O_3 and other colorant components.

We studied the specifics of glass formation in a multicomponent system $R_2O - Al_2O_3 - SiO_2 - TiO_2$ ($R = Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}$) and identified the regions of ceramic glass compositions in the system, for which purpose

we investigated the specifics of structure and phase formation of glass ceramic matrices in the given system.

TABLE 1

Glass matrix	Weight content, %								
	SiO ₂	Al ₂ O ₃	MgO	CaO	BaO	K ₂ O	Li ₂ O	Na ₂ O	TiO ₂
1	43.70	25.25	1.27	10.88	1.74	0.00	15.63	1.53	0.00
2	38.63	25.25	1.27	10.88	1.74	0.00	15.63	1.53	5.07
3	37.90	27.50	2.00	12.10	2.00	4.80	8.30	0.00	5.40
4	37.90	26.60	2.00	12.10	2.00	1.80	10.50	0.80	6.30
5	37.90	26.60	2.00	12.10	2.00	4.80	7.30	0.00	7.30
6	37.34	26.00	2.00	12.10	2.00	4.26	7.30	0.00	9.00
7	34.63	27.25	2.27	10.86	2.74	1.53	3.74	9.07	9.07
8	36.70	25.80	2.00	11.70	2.00	4.80	7.00	10.00	10.00
9	36.15	25.38	1.92	11.54	1.92	4.62	6.92	11.55	11.55
10	33.04	25.38	13.21	4.60	3.10	8.10	3.50	11.55	11.55
11	36.15	25.38	0.00	3.84	11.54	11.54	0.00	0.00	11.55
12	36.15	25.38	0.00	7.69	7.69	11.54	0.00	0.00	11.55
13	36.15	25.38	0.00	11.54	3.84	11.54	0.00	0.00	11.55
14	36.15	25.38	3.84	11.54	0.00	11.54	0.00	0.00	11.55
15	36.15	25.38	0.00	0.00	15.38	11.54	0.00	0.00	11.55
16	36.15	25.38	0.00	15.38	0.00	11.54	0.00	0.00	11.55
17	36.15	25.38	15.38	0.00	0.00	2.31	6.92	2.31	11.55
18	36.15	25.38	15.38	0.00	0.00	4.62	4.62	2.31	11.55
19	36.15	25.38	15.38	0.00	0.00	0.00	4.62	6.92	11.55
20	36.15	25.38	15.38	0.00	0.00	0.00	6.92	4.62	11.55
21	36.15	25.38	15.38	0.00	0.00	0.00	9.23	2.31	11.55
22	36.15	25.38	15.38	0.00	0.00	2.31	9.23	0.00	11.55
23	36.15	25.38	15.38	0.00	0.00	4.62	6.92	0.00	11.55
24	36.15	25.38	15.38	0.00	0.00	6.90	4.62	0.00	11.55
25	36.15	25.38	15.38	0.00	0.00	9.23	2.31	0.00	11.55
26	36.15	25.38	15.38	0.00	0.00	9.23	0.00	2.31	11.55
27	36.15	25.38	15.38	0.00	0.00	0.00	11.54	0.00	11.55
28	36.15	25.38	15.38	0.00	0.00	11.54	0.00	0.00	11.55
29	36.15	25.38	15.38	0.00	0.00	0.00	0.00	11.54	11.55

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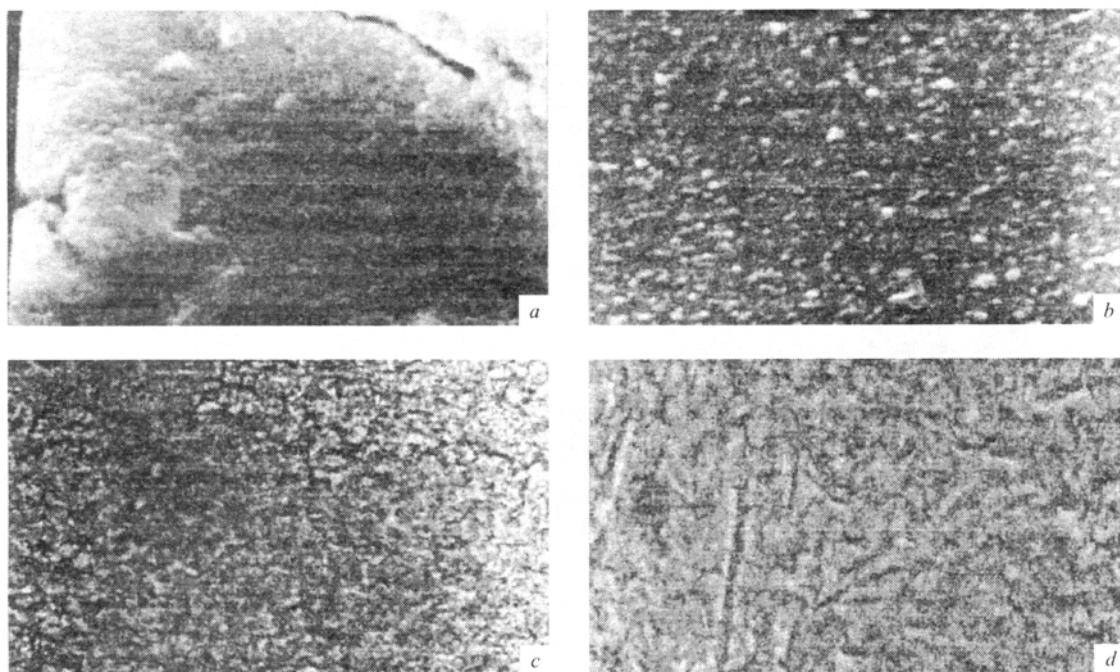


Fig. 1. Structure of ceramic glass matrixes: *a*) microliquation (530°C); *b*) pre-crystallization period (700°C); *c*) microcrystallization (860°C); *d*) completion of formation of glass ceramic structure with emergence of needle-

In order to select an optimum glass matrix composition, we used Tykachinskii's method which makes it possible in the first approximation to design glass ceramics with prescribed qualities.

The following requirements were imposed upon glass compositions:

In a repeated heat treatment, synthesized glass should crystallize by forming a light-colored coating;

Formation of a glass ceramic structure should be ensured;

TCLE value should be high, i.e., $(110 - 130) \times 10^{-7} \text{ K}^{-1}$.

In order to ensure the required crystallization conditions, it was necessary to find the optimum ratio of crystallization catalysts, which were TiO_2 and Li_2O . Their introduction facilitates the liquation of glasses intended for crystallization

and emergence of a glass ceramic structure. The developed glass matrix compositions calculated according to Tykachinskii are given in Table 1.

The reactant materials used to synthesize glass matrices and coatings produced on this basis were of "extra pure," "analytically pure," and "pure" grades. The glasses were melted in an electric furnace with Silit heaters and held for $2.5 - 3$ h at temperature $1300 - 1370^{\circ}\text{C}$.

The crystallizing capacity of glasses was studied by the mass crystallization method and the polythermal method in an electric muffle furnace at temperature $500 - 1000^{\circ}\text{C}$.

The study of the crystallizing capacity of glasses in heat treatment revealed the following (Table 2):

Arbitrarily complete bulk finely disperse crystallization in glass compositions 1 - 26 takes place at temperatures of

TABLE 2

Glass composition	Crystallization nature within the temperature interval, $^{\circ}\text{C}^*$				
	600 - 650	700 - 750	800 - 850	900 - 950	950 - 1000
1 - 26 Thin surface crystal film (below $10^3 \mu\text{m}$)	Intense surface crystallization, finely suspended in volume			Conventionally complete volume crystallization	
27 Crystallization is absent	Thin surface crystal film (below $10^3 \mu\text{m}$)		Intense surface crystallization	Intense surface crystallization and volume crystallization with large spherulites	
28	The same	The same	The same	The same	The same
29	The same	The same	The same	The same	Intense surface crystallization

800 and 1000°C, and the ante-crystallization processes occur at temperature of 50 – 700°C;

Crystallization of all glass compositions involves macroliquefaction;

In contrast to the generally known literature data, a glass ceramic structure was observed with a Li₂O content below 8%; a decrease to 6.3% is admissible.

Thus, with respect to crystallization, compositions 1 – 26 are the most suitable as glass matrices for glass ceramic coatings.

A thermographic analysis revealed the temperature intervals of crystallization and the temperatures for possible gradual treatment of glass:

I — 600 – 1600°C;
 $t_1 = 600, t_2 = 700, t_3 = 820, t_4 = 970, t_5 = 1060^\circ\text{C}$;

II — 530 – 960°C;
 $t_1 = 530, t_2 = 590, t_3 = 750, t_4 = 860, t_5 = 960^\circ\text{C}$;

III — 510 – 970°C;
 $t_1 = 510, t_2 = 600, t_3 = 650, t_4 = 760, t_5 = 970^\circ\text{C}$.

In order to determine the phase composition and the structure of glass ceramic matrices (Fig. 1), the samples were studied using x-ray phase analysis and electron microscopy.

It was found that glasses 27 – 29 under heat treatment form a microcrystalline structure which contains geikielite MgTiO₂, anorthite CaAl₂Si₂O₇, and a residual vitreous phase. A variety of crystalline phases is exhibited by matrix 25 in series II, which forms helenite Ca₂Al₂SiO₇; lithium metasilicate Li₂SiO₃; KMgSiO₄; nepheline KAlSiO₄, perovskite CaTiO₃; and ockermanite CaMgSiO₇.

The phases identified in glasses 1 – 22 were CaTiO₃, CaSiO₃, BaAlO₄, KAlSiO₄.

At the same time, a comparative analysis of IR-spectroscopic data revealed that glasses 13 – 26 which have a stable phase composition and, when heat-treated, are capable of forming a glass ceramic structure, have a specifically arranged silicon-oxygen frame based on mellite-type chains of various lengths consisting of linked structural groups [SiO₄]⁴⁻, [AlO₄]⁵⁻, [TiO₄]⁴⁻, and [MgO₄]⁴⁻ in the initial state, and [SiO₄]⁴⁻, [AlO₄]⁵⁻, [AlO₆]⁹⁻, [SiAlO₇]⁷⁻, [MgO₆]¹⁰⁻, and [TiO₆]⁸⁻ in the heat-treated state.

An extremely significant criterion in selecting a glass matrix for light-colored heat-resistant glass ceramic coating is its luminosity.

The study of several functional properties of the developed light-colored glass matrices determined their color characteristics. It was found that matrix 25 was clear before heat treatment and did not exhibit color shades, whereas after it was converted to glass ceramic, it acquired a milky-white color. The whiteness index was equal to 70%, as compared to the reference standard MS-20.

Based on the studied physicomechanical properties, as well as whiteness, the composition of glass matrix 25 was taken as the optimum one for heat-resistant light-colored glass ceramic coating. Its density was 2700 kg/m³, microhardness 4000 MPa, TCLE $115 \times 10^{-7} \text{ K}^{-1}$, and softening point 720°C.

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